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Additional Information

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6 **Remediation of a clay soil contaminated with phenanthrene by using**
7 **mixture of bentonite and cement**
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Remediation of a clay soil contaminated with phenanthrene by using mixture of bentonite and cement

Abstract:

This paper investigates the remediation of a clay soil contaminated with phenanthrene, through a series of experimental tests. Mixtures of bentonite-cement (with bentonite to cement ratios of 1:1 and 3:1) at 20 and 30% were used as agents. Unconfined Compressive Strength (UCS) tests were performed on samples with different percentages of agents and curing times. Leaching tests were also conducted on contaminated samples at different curing times by using spectrophotometer apparatus. The results indicated that using the mixtures of bentonite-cement as an agent for natural and contaminated soil leads to an increase in the strength of the soils. The results of leaching tests showed that, for a given percentage of bentonite-cement mixture with different bentonite to cement ratios, the concentration of phenanthrene decreased with increasing the curing time. The bentonite-cement ratio of 1:1 was found to be more effective than the 3:1 ratio in reducing the concentration of phenanthrene. Sensitivity analysis showed that the percentage of bentonite and curing time are more effective in the reduction of phenanthrene than the percentage of cement.

Keywords: Contaminated soil, Phenanthrene, Bentonite, Cement, Leaching test.

Introduction

Contaminants are referred to the substances that can be found either on or in ground and have potential to make pollution to specific receptors [1]. Contaminants can be divided into inorganic and organic groups. The base of inorganic contaminants is usually metals such as heavy metals, and they are often toxic. Organic contaminants have a carbon base and they are of greatest environmental concern. The source of organic contaminants is usually petroleum refineries, leakage from above or underground storage of petroleum products, and also accidents in their transportation.

Polycyclic aromatic hydrocarbons (PAHs) are a group of organic substances that are composed of nonpolar molecules that are made of two or more benzene rings. The United States Environmental Agency (U.S.EPA) has listed them as priority pollutants due to their toxicity and carcinogenic behavior [2]. Contamination of soil and groundwater by PAHs has been a serious problem worldwide. They are persistent in soils due to behaviors such as low water solubility and biodegradability and it is not easy to purge the soil from them [3]. Wild et al. [4] reported that this type of contaminated substances can remain in soil for more than 20 years. Phenanthrene is from the PAHs group and is one of the most contaminating substances that are found in large amounts in soil [5]. Therefore, remediation of soils contaminated with phenanthrene is important for the safety of the environment and the protection of groundwater resources. Stabilization and solidification (S/S) is an effective and relatively low-cost method for the remediation of contaminated soils [6]. In this method additives and binders are used to reduce the mobility and toxicity of the contaminating substances in soil [7]. Stabilization is a process in which chemical agents are used to reduce the potential of contaminant by changing it to a less toxic, less

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3 soluble, and less mobile form. Solidification is referred to a method in which a solid
4 material is made that encapsulates the contaminating substances. The solidification and
5
6 stabilization (S/S) method is usually used for the remediation of soils contaminated with
7
8 inorganic substances [8-17]. There is relatively limited experience in remediating soils
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10 contaminated with organic substances, particularly petroleum hydrocarbons, using S/S
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12 [18-20]. Cement and lime are common binders that are used for
13
14 stabilization/solidification but other binders such as pozzolan and silicate are also used, as
15
16 sometimes cement or lime are not effective in remediation of soils contaminated with
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18 organic substances. It has been indicated that some organic substances have a negative
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20 effect on the behavior of cementitious materials [21-23]. They may coat the particles of
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22 cement and prevent from chemical bonding of binder or make a weak bond. This can
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24 cause a reduction in compressive strength and durability of the stabilized soil [8]. When
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26 another binder is used together with cement, the detrimental effect of organic substances
27
28 may be reduced. Cioffi et al. [24] stated that using organoclay with cement can reduce the
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30 destructive behavior of organic compounds. Mohebbi et al. [25] used the S/S technique
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32 for remediation of a soil contaminated with cresol by adding a mixture of Portland
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34 cement and bentonite to it and found that the concentration of contaminated substance is
35
36 considerably reduced. Natali Sora et al. [23] reported that cement cannot effectively
37
38 immobilize 2-monochloroaniline (2-MCA) in a contaminated soil. They found that the
39
40 maximum release of 2-MCA in leachate solution was 75%. This indicated that cement, as
41
42 a binder, is not suitable and another binder should be examined. Therefore, an alternative
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44 method for increasing the efficiency of the S/S method for remediation of soils
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46 contaminated with organic substances is using another binder with the main binder
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3 (cement or lime). Leonard and Stegemann [26] reported that, by using a combination of
4 the main binder and another binder, an increase in sorption of an organic compound can
5 be achieved and it can also prevent from detrimental effects on the hydration of the
6 binders. Wang et al. [15] used mixture of MgO (Magnesia) and GGBS (Ground
7 Granulated Blast Furnace Slag) and Chen et al. [11] found that mixture of fly ash, MgO,
8 and GGBS are suitable binders for remediation of clay soils contaminated with organic
9 substances.

10
11
12 Ma et al. [27] showed that sulfonated oil can be successfully used for the remediation of
13 the soils contaminated with PAHs compounds. Söregård et al. [28] studied the
14 remediation of a soil contaminated with poly- and perfluoroalkyl substances (PFASs).
15 They examined the effect of seven different additives in the S/S treatment of soil. They
16 used the selected additives at 2% concentration. Overall, the S/S treatment with active
17 carbon based on the selected additives showed excellent performance in reducing the
18 leaching of PFASs. Kujlu et al. [29] studied the treatment of seven oil-contaminated soils
19 by using different additives. They reported that the highest and lowest leaching of
20 petroleum hydrocarbons corresponded to using diatomaceous earth (DE) and the
21 combination of Portland cement, sodium silicate, and DE (CS-DE), respectively. Feng et
22 al. [16] assessed the environmental performance of a roadway subgrade consisting of
23 contaminated soil solidified/stabilized with a hydroxyapatite-based binder (SPC) through
24 a field study. They used Portland cement (PC) as the control binder for comparison
25 purposes. They concluded that the SPC binder exhibited superior performance over PC in
26 terms of immobilization of Ni and Zn, soil pH, and curing time. Jebeli and Heidarzadeh
27 [30] reported that quick lime has enough potential for remediation a clay soil

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3 contaminated with phenol. Organic clays are usually used in the S/S technique for
4 remediation of contaminated soils with organic substances. Botta et al. [31], Zhu et al.
5 [32], and Heidarzadeh et al. [33] indicated that organophilic clays can be effective as an
6 adsorbent for hazardous organic waste. Al-Tabbaa and Perera [34] used a combination of
7 cement and organophilic clay as a binder for remediation of a soil that was contaminated
8 with hydrocarbons. Vipulanandan and Krishnan [35] reported that polyester polymer is
9 more effective than cement in the treatment of the contaminated soil. Estabragh et al. [36]
10 examined the use of cement (with different percentages) as a binder in the remediation of
11 a clay soil contaminated with MTBE (Methyl Butyl Ether). They found that cement is not
12 an effective binder in remediation and a combination of bentonite and cement can provide
13 more acceptable results.
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28 There have been relatively limited studies about the use of a mixture of bentonite and
29 cement as a binder for remediation of soils contaminated with organic compounds except
30 the work of [36]. In the S/S method, lime or particularly cement is usually used as a
31 binder. Recently, researchers have shown that some organic pollutants have a negative
32 effect on the performance of cement and prevent from the chemical reactions of its
33 binders [37-38]. On the other hand, in order to implement the S/S method for soils
34 contaminated with some organic contaminants high weight percentages of cement are
35 needed (Karamalidis and Voudrias [39] used cement as a binder for S/S experiments in
36 which the cement content varied from 10 to 70 %), which could be economically
37 unviable. In order to overcome these limitations of using cement as a binder, researchers
38 have suggested the use of binders that are a mixture of two or more materials such as
39 cement and bentonite or magnesium oxide and GGBS [15 and 25] They have reported
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3 that the results obtained by using these mixtures of binders are acceptable. This paper
4 presents a laboratory investigation into the remediation of a clay soil contaminated with
5 phenanthrene. The aim of the current investigation is to assess, for the first time, the
6 feasibility of using different mixtures of bentonite–cement for the remediation of a clay
7 soil contaminated with phenanthrene. Also, the effectiveness of this binder in reducing
8 the leachability of the contaminating substance in soil is studied. The effects of various
9 percentages of bentonite-cement and different bentonite to cement ratios (1:1 and 3:1) on
10 the remediation of a clay soil contaminated with phenanthrene are investigated. The
11 results obtained from different percentages of binders are analyzed, compared, and
12 discussed.
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26 **Materials and Methods**

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28 The materials that were used in this study including soil, cement, bentonite, and
29 phenanthrene. Their mechanical, physical, and chemical properties of them are as
30 follows:
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35 **Soil**

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37 A clay soil was used in this work. The physical and mechanical properties of the soil are
38 shown in Table 1. Based on the results from XRD (X-ray diffraction) tests, the soil was
39 composed of quartz, calcite, feldspar (Na, Ca), and feldspar (K) minerals. The clay
40 minerals of the soil were determined as illite, chlorite, and montmorillonite. Table 2
41 shows the chemical composition of this soil.
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49 **Cement**

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3 In this work, a Type 1 Portland cement with a specific gravity of 3.13 and Blaine
4 fineness of 4100 cm³/g was used. The physical and mechanical characteristics of the
5 cement were determined and the results are presented in Table 3.
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8 9 10 **Bentonite**

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12 A bentonite (Na-Montmorillonite) soil with high plasticity was used in this work. It was
13 composed of SiO₂, Al₂O₃, Fe₂O₃, MgO, CaO, Na₂O, K₂O, FeO, F, TiO₂, S, P₂O₃ and
14 traces with the percentages of 62.9, 19.6, 3.35, 3.05, 1.68, 1.53, 0.53, 0.32, 0.111, 0.09,
15 0.05, 0.049, and 0.006%, respectively. The organic content (O.C.) and CEC (Cation
16 Exchange Capacity) of the soil were determined as 0.072 % and 74.1 meq/100 g
17 respectively. The XRD tests showed that this soil was composed of quartz, calcite,
18 cristobalite, zeolite, dolomite, halite mineral, and with clay minerals of illite and
19 montmorillonite.
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22 **Agent (Binder)**

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24 The binder or agent to be added to the contaminated soil was prepared by mixing the
25 bentonite and cement. Mixtures of bentonite-cement (with bentonite to cement ratios of
26 1:1 and 3:1) were made as used by [36]. Contaminated soil was mixed with 20 and 30%
27 of this prepared mixture. The choice of bentonite as a part of the agent was due to its
28 ability to adsorb phenanthrene, as reported by [40].
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31 **Phenanthrene**

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33 The selection of phenanthrene was because it is widely used in industry, it is toxic and it
34 exists with high concentrations in soils, sediments, and waste sites [41]. The
35 phenanthrene that was used in this work was a product of Merck Company. The physical
36 and chemical behaviors of phenanthrene are listed in Table 4.
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Sample preparation

The contaminated soil was prepared in the laboratory by mixing air-dried soil with phenanthrene at concentration of 1200 mg phenanthrene/ kg of soil. Although according to the U.S.EPA [42], 500 mg/kg of PAH has been found near the surface of contaminated areas, in order to focus on the effect of phenanthrene on the behavior of soil and the used binder, a concentration of 1200 mg/kg was considered. The desired amount of phenanthrene was selected and dissolved in acetone (due to its low solubility in water). Then the solution of phenanthrene was mixed with air-dried soil according to the method that was used by Estabragh et al. [20] for making contaminated soil with anthracene. The prepared binders (bentonite and cement at bentonite to cement ratios of 1:1 or 3:1) were added to the natural and contaminated soil at percentages of 20 or 30%. Atterberg limits and compaction tests were performed on the natural soil, the contaminated soil, and the mixtures of the binder with them according to the ASTM (American Society for testing Materials) standard. Unconfined compressive strength (UCS) tests were conducted on samples of uncontaminated soil, contaminated soil, and mixtures of uncontaminated and contaminated soils with binders (at 20 and 30% percentage of binder) with various curing times. Preparing the samples for UCS test was done using the method that was used by Estabragh et al. [20 and 43]. After preparation, the samples were moved to a cabinet at constant temperature and relative humidity before they were tested similar to the method that was used by Kogbara et al. [44].

Experimental tests

The experimental tests that were conducted on the soil under various conditions are Atterberg limits, compaction, UCS, leaching and SEM (scanning electron microscopy).

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3 The Atterberg limits of used material were determined by conducting LL (Liquid limit)
4 and PL (Plastic limit) tests on the materials according to the ASTM standard. Compaction
5 tests were also conducted for the determination of the γ_{dmax} (Maximum dry unit weight)
6 and w_{opt} (Optimum water content). The main aim of conducting the UCS tests was to use
7 the results as an indicator, to determine the resistance of solidified and stabilized
8 materials against loading. Also, SEM tests were conducted to study the microstructure of
9 the soil under different conditions (different percentages of binders). Leaching tests were
10 used to determine the leachability of the contaminating substance for various percentages
11 of binders with different ratios and at various curing times. Fig.1 shows a schematic
12 diagram of tests that were conducted for S/S of the contaminated soil. A brief description
13 of these experimental tests is as follows:

24 **Atterberg limits and compaction tests**

25 Atterberg limit tests were performed according to the ASTM standard to find the values
26 of LL (Liquid limit), PL (Plastic limit) and PI (Plastic index) of the soils. Compaction
27 parameters including γ_{dmax} and w_{opt} were determined from standard compaction tests.

28 **Strength tests**

29 The aim of conducting UCS tests was to find the effect of used binders on the treatment
30 of contaminated soil. The tests were performed on samples with various binder contents
31 at different curing times according to ASTM standard. Details of the procedure for the
32 UCS test can be found in [45].

33 **Leaching tests**

34 The method proposed by U.S.EPA (United State Environmental Protection Agency) [46]
35 was used for conducting the leaching tests on samples of contaminated soil treated by

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3 different percentages of agents at different curing times. The compacted cylindrical
4 samples at different curing times were pulverized to small particles (less than 9.5 mm).
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6 The particles were then mixed with distilled water with ratio of 16:1 and the value of pH
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8 for this mixture was measured at time intervals of 15, 30 and 60 minutes. To keep the
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10 value of pH for this mixture around 5, acetic acid with normality of 0.5 and with a mass 4
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12 times the mass of solid particles was added to the mixture (according to U.S.EPA
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14 standard) and was placed in a shaker for 24 hours then the pH of it was measured again.
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16 Then appropriate amount of distilled water was added to dilute the mixture so that the
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18 ratio of solid to liquid became 1:20. This mixture was placed on a shaker for 4 hours then
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20 it was moved on a table with flat surface so that the liquid and solid phases were
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22 separated from each other by settlement of the solid particles. The liquid phase was then
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24 passed through a filter with mesh size of 0.45 μm and suspended materials were removed
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26 from the liquid section. An Alpha 1900S Double spectrophotometer was used to
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28 determine the presence of phenanthrene in the prepared liquid. After calibration of the
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30 apparatus and determination of the wavelength for absorption the phenanthrene, it was
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32 found that the wavelength of phenanthrene is 250 nm. Then different liquid solutions of
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34 phenanthrene were placed in the apparatus and the amount of absorption was determined
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36 for each sample.
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44 **SEM tests**

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46 SEM tests were conducted on samples prepared from different materials at a curing time
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48 of 28 days. The results obtained from these tests were used for assessing the effect of
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50 microstructure on the behavior of uncontaminated and contaminated soil with different
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52 percentages of binders. The samples were pulverized to small particles and they were
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3 dried by using a vacuum apparatus. Then they were moved on metal stubs, sputter coated
4 by gold and then placed on the apparatus. The apparatus that was in this work was
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6 HITACHI model S-4160.
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9 10 **Results**

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12 The results obtained from the above tests are presented in the following sections.
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14 **Atterberg limits and compaction parameters**

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16 Table 5 presents the results of the Atterberg limits and compaction tests for different
17 materials used in this work. It is observed from this table that the LL, PL, and PI for the
18 natural soil are 47, 26, and 21 % respectively. By adding 20 and 30% mixture of
19 bentonite and cement with the ratio of 1:1 they are increased. For example, by adding
20 30% bentonite-cement mixture, the values of LL, PL and PI are changed to 62.0, 33.0,
21 and 29.0 % respectively, showing that they all increase in comparison with the natural
22 soil. The values of LL, PL, and PI for the contaminated soil are 50, 27, and 23%
23 respectively (Table 5) and they are increased by adding the mixture of bentonite-cement.
24 The results show that the values of Atterberg limits are higher for the samples with 30%
25 mixture of bentonite-cement (with bentonite-cement ratio 1:1) compared with those with
26 20% bentonite-cement mixture. In addition, for the same percentage of the bentonite-
27 cement mixture, the values of Atterberg limits for bentonite-cement ratio of 3:1 are more
28 than the ratio of 1:1, for both uncontaminated and contaminated soils. The results in
29 Table 5 show that the γ_{dmax} and w_{opt} of the natural soil are 16.77 kN/m³ and 18.5%
30 respectively. However, by adding 20% mixture of bentonite-cement with ratio of 1:1, the
31 values of γ_{dmax} and w_{opt} are increased and decreased while they decrease by adding 30%
32 bentonite-cement mixture. The γ_{dmax} and w_{opt} for the contaminated soil are 16.8 kN/m³
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3 and 16.0% respectively, but by using the mixture of bentonite-cement the γ_{dmax} is
4 decreased and w_{opt} is increased. Comparison of the results in this table shows that, for a
5
6 given percentage of bentonite-cement mixture, the changes in the two compaction
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8 parameters are more for the mixture of bentonite-cement with the ratio of 3:1 than the
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10 ratio of 1:1.
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14 **Strength**

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17 Fig.2 shows typical results of stress-strain curves for the natural soil, contaminated soil,
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19 and natural soil with 20% bentonite-cement mixture with the ratio of 1:1 at different
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21 curing times. It is seen from this figure that the natural soil has a final strength of 271.5
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23 kPa. But with the bentonite-cement mixture, it changes to 1798, 2907, 3917, and 4671
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25 kPa at curing times of 3, 7, 14, and 28 days respectively.
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29 Fig.3 shows the final strengths of the samples against curing time for the natural soil and
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31 contaminated soil with 20 or 30% mixture of bentonite-cement with the ratio of 1:1 or
32
33 3:1. As shown in this figure, for a given percentage of these binders the strength increases
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35 with increasing the time of curing. It is also seen that, for both uncontaminated and
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37 contaminated soils, the final strength of the samples with bentonite-cement mixture with
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39 the ratio of 3:1 is less than the ratio of 1:1.
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42 **Leaching**

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45 Figs.4a and b show the results of the leaching tests that were obtained from the
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47 spectrophotometer apparatus for the contaminated soil and the contaminated soil with 20
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49 and 30% bentonite-cement mixture with the ratios of 1:1 and 3:1, respectively. The
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51 results in Fig.4a indicate that the concentration of the soil contaminated with
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53 phenanthrene is 32.27 mg/kg but it is decreased by adding different percentages of
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3 mixture of bentonite-cement with the ratios of 1:1 or 3:1 and different curing times. As
4 shown in this figure, by adding 20% mixture of bentonite-cement with ratio 3:1, the
5 concentration of phenanthrene is changed to 7.47, 3.148, and 0.124 mg/kg at curing times
6 of 7, 14, and 28 days respectively. By using 30% mixture of the binder with the ratio of
7 3:1, the reduction in concentration is less than 20% mixture at different curing times (Fig.
8 4b). The results in Fig. 4b also indicate that the effect of 20 or 30% 1:1 mixture on the
9 reduction concentration of phenanthrene is more than the same percentage for 3:1
10 mixture.
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22 SEM

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24 Fig. 5 shows the micrographs for the natural soil and the mixture of the natural soil with
25 different percentages of bentonite-cement at the curing time of 28 days. Fig. 5a shows the
26 SEM image of the natural soil that is composed of particles with different sizes without
27 any bonding between them. Typical images for 20 or 30% bentonite-cement with ratios
28 of 1:1 and 3:1 are shown in Figs. 5b, c, d, and e. The hydration products are seen only in
29 Figs.5c and e in the spaces between the particles that interconnect them. The micrographs
30 of the contaminated soil and mixture of contaminated soil with different percentages of
31 bentonite-cement with ratios of 1:1 and 3:1 are seen in Fig.6. Fig.6a shows the SEM
32 image of the contaminated in which the soil particles are in the form of sheets and nearly
33 parallel to each other without any bonds between them. The hydration products are seen
34 in Figs.6b, c, and e in the spaces between the particles.
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49 Discussion

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51 The minerals of clay are plate like in shape, with high specific surface. These physical
52 characteristics of clay minerals result in high efficiency of electrical forces between the
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3 particles. Particles of clay usually carry negative charges on their surface [47]. This
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5 charge is resulted from the high specific surface of the particles and isomorphous
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7 substitution. Isomorphous substitution occurs when an element with lower positive
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9 valance is substituted with a higher valance one and these results in negative charge on
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11 the clay minerals. When the dry soil is mixed with water, the positive ions in water are
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13 attracted to the negative ions on the particles of clay to make a balance in concentration
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15 of ions. The negative charges of clay particles limit the diffusion of the cations, leading to
16
17 the distribution of ions around the clay particles. This configuration of ions around the
18
19 clay particles is called diffuse double layer (DDL) which has an important role in creating
20
21 different structures (flocculated or dispersed) in soil.
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26 Contaminant substances can be adsorbed by clay particles in the form of physical or
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28 chemical adsorption. In the case of physical adsorption, the contaminant in the pore fluid
29
30 is attached to the surface of soil particles due to Van der Waals forces and it is marked as
31
32 low energy adsorption. Chemical adsorption or chemisorption occurs due to the creation
33
34 of permanent chemical bonds between contaminant substance and soil particles. Factors
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36 such as shape, size, polarizability, and water solubility of organic contaminants have an
37
38 important effect on their adsorption by soil. Yong [48] stated that the adsorption of
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40 organic substances to soil particles can also be via Van der Waals, hydrophobic reaction,
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42 hydrogen bonding, charge transfer, or ion exchange.
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46
47 Table 5 shows that the LL, PL, and PI of the natural soil are 47.0, 26.0, and 21.0%
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49 respectively. The values of Atterberg limits are increased by adding the mixture of
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51 bentonite-cement with ratio of 1:1 to the natural soil (Table 5). It is also shown that
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53 adding 30% bentonite-cement mixture with 1:1 ratio is more effective than the 20%
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3 mixture in increasing the values of Atterberg limits. The LL, PL, and PI for the
4 contaminated soil are 50.0, 27.0, and 23.0% respectively (Table 5) that are slightly higher
5 than the natural soil. When the mixtures of bentonite-cement with the ratios of 1:1 and
6 3:1 are added to the contaminated soil, the values of Atterberg limits are increased in
7 comparison with those of the contaminated soil. The results also show that the effect of
8 bentonite-cement mixture with the ratio of 3:1 is more than the mixture with the ratio 1:1
9 in increasing the Atterberg limits. It can be resulted that the changes in the Atterberg
10 limits of the contaminated soil are also a function of the percentage of the used mixture
11 and the ratio of bentonite to cement in the mixture. The adsorption of the contaminant
12 creates more voids between the particles in comparison with the natural soil as shown in
13 Figs. 5a and 6a. This can increase the values of Atterberg limits compared with the
14 natural soil. The increase in the Atterberg limits of the natural soil and contaminated soils
15 that were mixed with bentonite-cement is due to the characteristics of bentonite.
16 Bentonite has a high plasticity and high potential to adsorb water. This can be the main
17 reason for increasing the Atterberg limits. It is seen that the bentonite-cement mixture
18 with the ratio 3:1 is more effective than the mixture with the ratio 1:1 in increasing the
19 Atterberg limits of the soil.

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22 It is observed from Table 5 that, the γ_{dmax} and w_{opt} of the natural soil are 16.77 kN/m³ and
23 18.5% respectively. These compaction parameters for the natural soil with 20 or 30%
24 bentonite-cement mixtures with ratios 1:1 or 3:1 show no specific trend in relation to the
25 natural soil (Table 5). Table 5 shows that the γ_{dmax} and w_{opt} of the contaminated soil are
26 16.8 kN/m³ and 16% respectively. When the mixtures of bentonite-cement with ratios of
27 1:1 and 3:1 with different percentages are added to the contaminated soil, the γ_{dmax} is

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3 decreased and the w_{opt} is increased. This can be due to the creation of more pore spaces in
4 the contaminated soil (Fig. 6a) and filling of a part of these spaces by the bentonite-
5 cement mixture. As mentioned above, the potential of bentonite in adsorption of water is
6 relatively high and this causes increase in the w_{opt} and decrease in the γ_{dmax} . These results
7 are different from those that were reported by [44]. The reason of it may be due to the
8 type of contaminants and binders that were used by them.
9

10 Fig. 2 shows that the final strength of the soil contaminated with phenanthrene is less
11 than the natural soil. The results obtained are in agreement with those that were reported
12 by Estabragh et al. [36 and 49] and Ratnaweera and Meegooda [50]. But these
13 researchers stated that their results were in contradiction to the assumptions of the DDL
14 theory. They believed that the change in the viscosity of pore fluid can affect the strength
15 of soil. However, increasing the viscosity of pore fluid facilitates displacement of the
16 particles which leads to the reduction of strength. In this work, the reduction in the
17 strength of contaminated soil can be explained by changing the structure of the soil due to
18 the phenanthrene. Figs. 5a and 6a show the micrographs of the natural soil and the soil
19 contaminated with phenanthrene. As shown in Fig.5a, the structure of the natural soil is in
20 a flocculated form but by adding phenanthrene to the soil, the degree of flocculation is
21 decreased and the particles are changed to a lamellar form without friction between them
22 (Fig.6a). The change in the structure of the soil can be due to the chemical reaction of
23 phenanthrene with pore water. The hydrolysis of phenanthrene in pore water may
24 produce an acidic aqueous condition which can break the bond between the particles of
25 soil and change them to smaller particles. As shown in Fig.6a, the friction between the
26 particles is less in the contaminated soil than the natural soil. The structure of the
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3 contaminated soil includes larger pores than the natural soil (Fig.5a). Therefore the
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5 contaminated soil is more compressible, and its strength is less than the natural soil.
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8 The results in Fig.2 also show that adding the mixture of bentonite-cement with the ratio
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10 of 1:1 (bentonite to cement) at 20% to the natural soil increases the final strength and the
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12 amount of increase is a function of curing time. When cement is mixed with a clay soil
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14 and water is added to it, hydration of the cement occurs rapidly. One of the major
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16 hydration products is hydrated lime. The reaction of the carbon dioxide in soil, air, and
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18 pore water produces carbonic acid. The reaction results in the dissociation of lime into
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20 Ca^{+2} and OH^{-1} . The change in the structure of the soil is a consequence of the cation
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22 exchange of monovalent alkali ions dissociated with divalent calcium ions in the pore
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24 water. This would lead to a flocculated structure in the soil and a reduction in its
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26 plasticity. Kézdi [51] also stated that during the hydration of cement, the pH of pore fluid
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28 is raised and hence it can solve the alumina and silica of minerals of the soil. The hydrous
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30 of silica and alumina will then gradually react with calcium ions liberated from the
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32 hydrolysis of cement to form insoluble compounds that are known as pozzolanic reaction.
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34 The pozzolanic reaction that takes place in soil-cement produces cementitious products
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36 such as portlandite, ettringite, calcium silicate hydrate (CSH), and calcium aluminate
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38 hydrate (CAH) ([51]). The increase in the strength of soil-cement with time is mainly due
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40 to pozzolanic reactions. These gels bind the soil particles and develop a strong linkage
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42 between the minerals and the aggregates to form a structure whereby the particles of soil
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44 can no longer slide over each other. Therefore, not only does cement destroy the soil's
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46 plasticity, but it also increases its strength. These results are consistent with the results
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48 that were reported by Estabragh et al. [36].
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3 Fig. 3 shows the changes of the final uniaxial compressive strength with curing time for
4 the uncontaminated and contaminated soils with 20 and 30% bentonite-cement mixtures
5 by the ratios of 1:1 and 3:1. The results in this figure are obtained based on the final
6 strength from the stress-strain curves of different tests. In all cases, the increase in the
7 strength of soil is associated with increasing the curing time (Fig. 3). It is seen that using
8 20% bentonite-cement with the ratio of 1:1 is more effective than 30% of this mixture in
9 increasing the strength of the natural soil. A similar trend is seen in Fig. 3 for the mixture
10 of bentonite-cement with the ratio of 3:1. Comparison of the results for the treated natural
11 soil indicates that the strength of the soil with 20 or 30% bentonite-cement mixture with
12 the ratio of 1:1 is more than the mixture with ratio of 3:1. As mentioned above, the ion
13 exchange capacity of bentonite is very high. When the mixture of bentonite and cement is
14 added to the soil, the exchange of ions with the bentonite is more than the natural soil.
15 Therefore, the released calcium ions from the cement can be exchanged with soil and
16 bentonite. As it was explained these processes are led to the production of cementitious
17 materials such as CSH and CAH (Figs. 5c and 5e). These produced materials cause the
18 strong bonds between the particles resulting in increasing the strength of soil. The results
19 also show that the use of 30% bentonite-cement mixture has less effect on the strength
20 than the 20% mixture. By using 30% bentonite-cement mixture, the amount of bentonite
21 and cement in the soil is more than the case of 20% mixture. It may be that a part of
22 bentonite produces dispersed structure between particles due to repulsive forces and
23 causes a reduction in the friction between particles and the bonds between them. These
24 bonds are not as strong as the bonds that are created by hydration products of cement and
25 a reduction in the friction between particles can cause a reduction in the strength.
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3 Comparison of the results shows that, at a given percentage of binder, the strength of the
4 soil mixed with the binder with the ratio of 3:1 is less than 1:1. In this case, the amount of
5 bentonite with the ratio of 3:1 is more than the ratio of 1:1. Increasing the amount of
6 bentonite causes more cement to adsorb to it and some of the bentonite produces
7 dispersed structure and weak bonds between soil particles. Therefore, a lower ratio of
8 bentonite to cement contributes to making the cementitious materials that increase the
9 strength of the soil. The variations of strength for the contaminated soil treated with
10 mixtures of bentonite-cement with different ratios and percentages are also shown in Fig.
11 3. It is observed from this figure that the strength of the contaminated samples treated
12 with mixtures of bentonite-cement at various ratios is increased with increasing the
13 curing time and the rate of increase in strength is less than the natural soil treated with
14 these mixtures. This could be because, in the case of the contaminated soil, some of the
15 soil particles are covered by phenanthrene due to adsorption which could prevent from
16 the formation of strong bonds between soil particles and the produced cementitious
17 materials ([39]). On the other hand, as shown in Fig.6a, the particles of contaminated soil
18 are nearly parallel with dispersed structure in comparison with the microstructure of
19 natural soil (Fig.5a). In this type of structure, the space between particles is less than the
20 natural soil, limiting the penetration of the cement products between them. Therefore,
21 these factors are important in reducing the strength of contaminated soil. Estabragh et al.
22 [36] found results similar to these obtained results. The results (Fig. 3) also indicate that
23 for the contaminated soil, the strength of the sample with 30% bentonite-cement at the
24 ratio 1:1 is more than with 20% mixture at the same ratio. The same trend is also seen for
25 the mixtures at 20 and 30% with the ratio of 3:1, but the strength of the samples treated
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3 by mixtures with the ratio of 1:1 is more than the ratio of 3:1. These variations of strength
4 are in the opposite direction of the treated natural soil. It can be said that, in the case of
5 contaminated soil, some soil particles are covered with phenanthrene and also due to
6 dispersed structure (Fig. 6a) which limits the reaction between them and cement.
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8 Therefore, by using 20% of this mixture, some of the cement is adsorbed to the bentonite
9 and less cement is available for the pozzolanic reaction. However, with 30% mixture,
10 more cement is available for the pozzolanic reaction which increases the strength. It is
11 also seen that the strength of mixtures of 20 and 30% of binder with the ratio 1:1 is more
12 than the ratio 3:1. It may be that in this case, a part of the cement reacts with bentonite
13 and the rest makes weak bonds between soil particles. This results in reduction of the
14 strength in comparison with the mixture with 1:1 ratio.

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28 Figs.4a and b show that the mixtures of bentonite-cement with different ratios and
29 percentages are effective in reducing the concentration of phenanthrene in the
30 contaminated soil. As shown in these figures, for a constant percentage of bentonite-
31 cement with a specific ratio, increasing the curing time is effective in the reduction of the
32 contaminant in the soil. It is seen from these figures that increasing in the percentage of
33 binder (at the same bentonite-cement ratio) causes more reduction in the concentration of
34 phenanthrene. Also, at a constant percentage of binder, the bentonite-cement with the
35 ratio of 1:1 is more effective than the ratio of 3:1. It is concluded from this figure (Fig.4)
36 that the combination of bentonite and cement is effective in reducing the concentration of
37 phenanthrene because of the adsorption of phenanthrene, particularly by bentonite ([40])
38 and cement. The particles of clay soil and bentonite may adsorb a major part of
39 phenanthrene or phenanthrene can be deposited as a salt between the spaces of particles
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3 due to the chemical reactions. Adsorption of contaminant to soil particles is called
4 surficial attachment ([48]) and can be physical or chemical adsorption. The properties of
5 organic contaminants are different from the soil. Therefore, the characteristics of organic
6 contaminants that are important in adsorption to soil are shape, size, polarity and water
7 solubility. Leonard and Stegemann [26] and Zampori et al. [52] stated that the binding
8 mechanisms between binders and organic compounds are physical entrapment in the
9 produced matrix and sorption on the surface of hydration products rather than chemical
10 reaction. Yong [48] indicated that the mechanisms for binding organic chemicals can be
11 through Van der Waals hydrophobic reaction, hydrogen bonding, charge transfer, and ion
12 exchange. Figs. 4a and b show that the majority of reduction in the concentration of
13 phenanthrene occurs at early stage of curing and the amount of reduction is increased by
14 increasing the percentage of mixture of bentonite-cement and reducing the bentonite to
15 cement ratio. This is because at higher percentage of bentonite-cement mixture more
16 CSH and CAH are produced resulting in greater reduction in concentration. Therefore,
17 the percentage of the used mixture, the ratio of bentonite to cement, and the curing time
18 are the main factors influencing the removal or encapsulation of phenanthrene. It can be
19 said that adsorption and encapsulation are important in the reduction the concentration of
20 contaminant. As shown in Fig. 4, the binder with the ratio of 1:1 is more effective than
21 the ratio of 3:1. This indicates that with the bentonite-cement the ratio of 1:1, the
22 encapsulation of phenanthrene by cement is more than the ratio of 3:1. In this mechanism,
23 the results in Fig.4 also show that after 14 days of curing, the rate of reduction in
24 concentration is not significant. After 14 days, the produced hydration products result in
25 encapsulation of the contaminant. The hydration products are able to accommodate a
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3 wide variety of extraneous cations as well as organic compounds by hydrogen bonding,
4 hence providing an excellent host for contaminants ([3]). Fig.7 shows a schematic
5 diagram of different stages of the S/S technique and its mechanism. As shown in this
6 diagram, S/S involves immobilization of the contaminants through reactions with
7 additives and binders by adsorption and precipitation mechanisms instead of removing
8 them. This occurs by hydration products such as CAH and CSH. Therefore, this process
9 reduces the mobility and leaching, as well as the toxicity level and solubility of the
10 contaminants.
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12 Bone et al. [53] stated that the main reactions between contaminants, pore water, and soil
13 are sorption, precipitation, and hydrolysis. Organic matters interact with clays by
14 adsorption onto the surfaces of clay soil by hydrogen bonding, ion exchange, and
15 intercalation. Adsorption of organic matter onto the clay particle surface depends on the
16 availability of the surface and the ability of the organic molecules to displace water
17 molecules. Adding the mixture of bentonite-cement to the contaminated soil causes a
18 reduction in the concentration of phenanthrene. This reduction is dependent on the
19 percentage of this mixture, the ratio of bentonite to cement, and curing time. The higher
20 the percentage of this mixture, and curing time, the higher is the reduction in
21 concentration of phenanthrene (Fig.4). This observation suggests that the mechanism
22 responsible for the removal or encapsulation of phenanthrene is dependent on time and
23 percentage of used binder. This time dependent behavior of phenanthrene is difficult to
24 explain as it may be the result of several concurrent and counteracting phenomena such
25 as degradation, desorption from clay minerals, and encapsulation of the compounds.
26 Karamalidis and Voudrias [39] used the encapsulation phenomenon to explain the effect
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3 of stabilization and solidification of an oil refinery sludge. The subsequent decrease of
4 concentration observed in some cases suggests that progressively tighter encapsulation of
5 the compounds in the clay aggregates (produced by pozzolanic reactions) may become
6 dominant after longer curing time and with increasing the percentage of binder. Therefore,
7 the higher degree of immobilization of the organic matter is due to the amount and type
8 of produced hydration products. Leonard and Stegemann [26] stated that high organic
9 contaminants in a soil can prevent from producing the binder materials. They can also
10 produce considerable micro and macro structural changes to the hydration products and
11 affect the mechanical behavior of remediated contaminated soil.
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24 The S/S method involves immobilization of contaminants through reactions with
25 additives and binders by adsorption and precipitation mechanisms instead of removing
26 them. This occurs by hydration of the bentonite-cement mixture and production of new
27 products such as CSH, CAH and ettringite. Therefore, this process reduces the mobility
28 and leaching, as well as the toxicity level and solubility of the contaminants. The
29 reduction in the concentration of the contaminant by increasing the curing time may be
30 due to the progressive encapsulation of contaminating material by the production of new
31 products such as CSH, CAH, and ettringite that become more significant with increasing
32 the curing time and by increasing the percentage of bentonite-cement mixture. These
33 results are in agreement with the results that were published by Mohebbi et al. [25]. They
34 found from the results of experimental tests that adding modified clay in soil
35 contaminated with cresol resulted in a decrease in the amount of cresol leaching from S/S
36 products as compared to the contaminated soil. Lo et al. [54] reported that organoclay is
37 able to remove the organic pollutants from the contaminated soil and their results are in
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3 agreement with those obtained in the present research. Belarbi and Al-Maleck [55]
4 reported similar results for the remediation of a clay soil contaminated with phenol, by
5 using a clay soil modified by a cationic surfactant.
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10 The World Health Organization/International Program on Chemical Safety (WHO/IPCS)
11 ([56]) indicated that the acceptable level of PAHs components in soil is between 1-3
12 mg/kg. The results of this work showed that with 20 and 30% of bentonite-cement with
13 the ratio of 3:1 the remaining phenanthrene in the soil reached to 0.12 and 0.09 mg/kg
14 respectively after curing time of 28 days. The results also indicated that for bentonite-
15 cement with the ratio of 1:1 at percentages of 20 and 30% the final values of remaining
16 phenanthrene in soil are 0.08 and 0.052 mg/kg for curing time of 28 days. These values
17 are less than the range of acceptable values recommended by WHO/IPCS and hence, the
18 contaminated soil with these levels of phenanthrene would not be harmful to the
19 environment.
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32 **Statistical Analysis**

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35 The purpose of the statistical analysis is to determine the roles and degrees of importance
36 of percentage of cement, bentonite and curing time in remediation of contaminated soil.
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38 Many forms of MNLR (Multiple Non-Linear Regression) equations were examined and
39 the following regression equation was suggested for the calculation of concentration of
40 phenanthrene:
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$$46 \quad y = \beta_0 + \beta_1 x_1^2 + \beta_2 x_2^2 + \beta_3 x_3^2 + \beta_4 x_1 x_3 + \beta_5 x_2 x_3 + \beta_6 x_1 x_2 x_3 + \beta_7 x_1 + \beta_8 x_2 + \beta_9 x_3 \quad (1)$$

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48 where y is the dependent variable, x_1 , x_2 and x_3 are the independent variables and β_0
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50 to β_9 are the regression coefficients. The regression coefficients were determined by
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52 specifying the values of independent and dependent variables in a matrix form and then
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3 solving the set of equations. Based on the experimental data points for the percentages of
4 cement (x_1) and bentonite (x_2) and curing time (x_3) the obtained regression equation for
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6 concentration of phenanthrene is as follows:
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$$9 \quad y = 32.27 + 0.02x_1^2 + 0.12x_2^2 + 0.02x_3^2 + 0.08x_1x_3 + 0.16x_2x_3 - 0.01x_1x_2x_3 - 0.79x_1 \quad (2)$$

$$10 \quad -3.04x_2 - 2.27x_3$$

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15 It should be said that the percentages of bentonite and cement for using 20 and 30% of
16 this mixture with the ratio 1:1 (bentonite:cement) were 10% bentonite and 10% bentonite
17 and 15% bentonite with 15% cement. These values for the above percentages of mixture
18 with the bentonite:cement ratio of 3:1 are changed to 15% bentonite and 5% cement for
19 usage of 20% mixture and 22.5 and 7.5% for 30% of this mixture.
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26 Fig.8 shows the measured concentrations against the predicted values. The values of
27 coefficient of determination (R^2) and Root Mean Square Error (RMSE) are equal to
28 0.9997 and 0.146 respectively. The value of R^2 shows a high correlation between the
29 measured and predicted concentrations. RMSE is a measure of the fitness of a model and
30 represents the differences between the predicted and observed values. RMSE has the
31 same units as the quantity being estimated for an unbiased estimator. Its range of
32 variations is between 0 to an unknown value. A lower value of RMSE would indicate a
33 better fitting of the proposed regression model with the data. The degree of influence of
34 each parameter on the value of concentration (sensitivity index, $S(X_i)$) for the above
35 equation can be calculated from the following relationship.
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$$49 \quad S(x_i) = \frac{\sigma(x_i)}{n\sigma(y_i)} \sum_{j=1}^n \left| \frac{\partial y}{\partial x_i} \right| \quad (3)$$

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3 where $S(x_i)$ is the degree of significance of the independent variable x_i in calculating
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5 the dependent variable y and n is the number of data points. $\sigma(x_i)$ and $\sigma(y_i)$ are the
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7 measured and predicted data in x and y directions. $\frac{\partial y}{\partial x_i}$ is the partial derivative of y with
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9 respect to x_i . Based on the above equation, the degree of significance for effects of
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11 percentage of cement, percentage of bentonite, and curing times were calculated as 25.9,
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13 41.8, and 32.3% respectively. By comparing these results, it is concluded that, the
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15 percentage of bentonite and curing time have more effect than the percentage of cement
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17 on concentration of phenanthrene during leaching.
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24 **Conclusion**

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26 The stabilization and solidification technique was studied for remediation of a clay soil
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28 contaminated with phenanthrene through a set of experimental tests. The conclusions
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30 drawn from this work are as follows:
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- 33 - Using a mixture of bentonite-cement as a binder is effective in increasing the strength
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35 of natural and contaminated soil. The amount of increase in strength of both
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37 contaminated and natural soils is a function of the percentage of bentonite-cement,
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39 bentonite to cement ratio, and curing time. The increase in strength is less for the
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41 contaminated soil than the uncontaminated soil.
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- 44 - These agents are effective in reducing the concentration of phenanthrene in leaching
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46 tests and the rate of reduction is decreased with increasing the curing time. The mixture
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48 of bentonite-cement with the ratio of 1:1 is more effective in reducing the concentration
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50 of phenanthrene in comparison with the 3:1 mixture.
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3 - It was found from sensitivity analysis the percentage of bentonite and curing time are
4 more effective in reducing the concentration of phenanthrene than the percentage of
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6 cement
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10 **Conflict of interest**

11
12 There is no conflict of interest in this paper.
13

14 **Author contributions**

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16
17 **A.R. Estabragh:** Conceptualization (lead); data curation (equal); formal analysis (lead);
18 investigation (lead); methodology (lead); Supervision (lead); validation (lead); writing-
19 original draft (lead); Writing -review & editing (lead). **M. Amini:** : Conceptualization
20 (equal); data curation (lead); formal analysis (equal); investigation (equal); methodology
21 (equal); validation (equal); writing-original draft (equal); Writing -review & editing
22 (equal). **A.A. Javadi:** : Investigation (equal); supervision (equal); writing-original draft
23 (supporting); Writing -review & editing (equal). **C. Lull Noguera:** Investigation (equal);
24 methodology (equal); supervision (equal); writing-original draft (supporting); Writing -
25 review & editing (equal).
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38 **Availability of data**

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40 The datasets used and/or analyzed during the current study are available from the
41
42 corresponding author on reasonable request.
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44

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49 research work.
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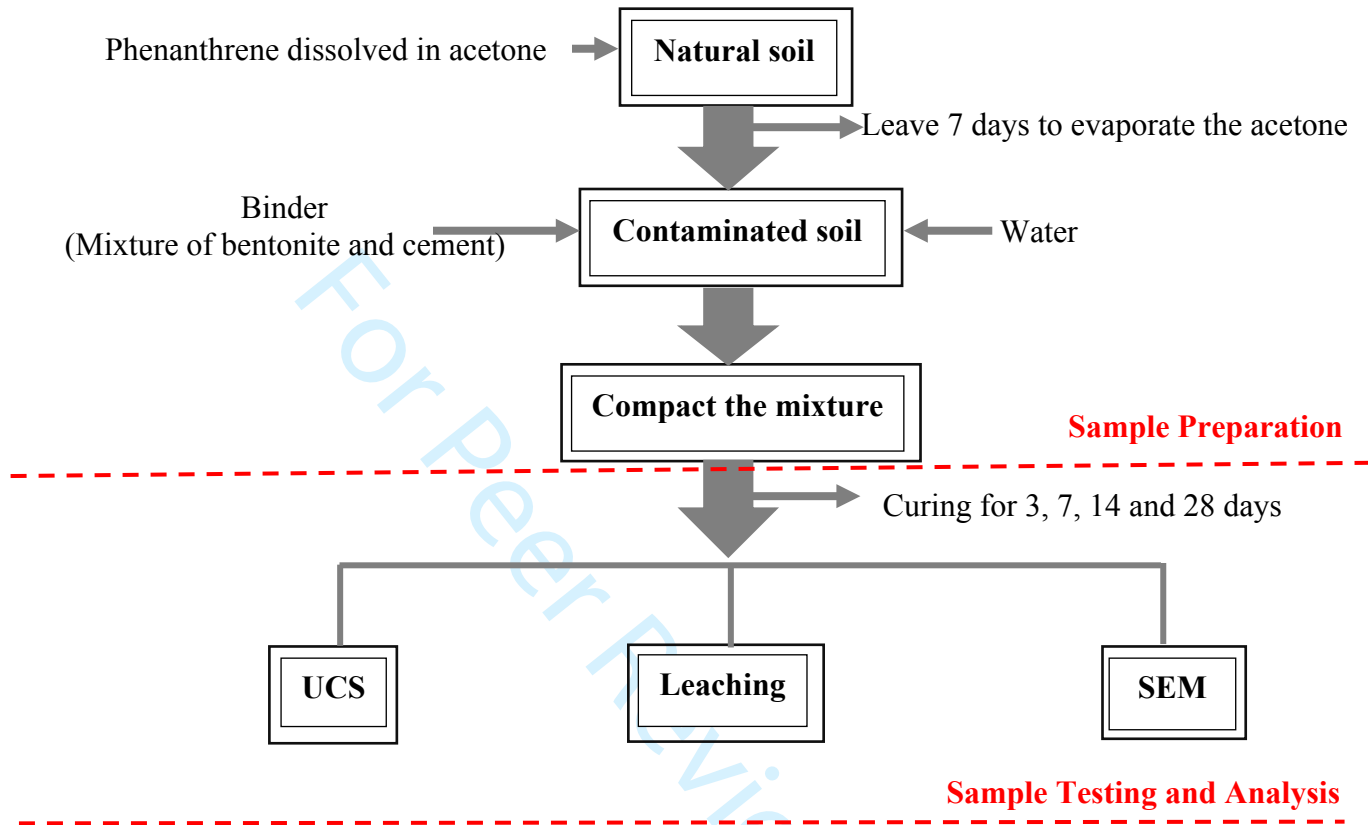


Fig.1. Schematic diagram of stabilization and solidification of phenanthrene contaminated soil

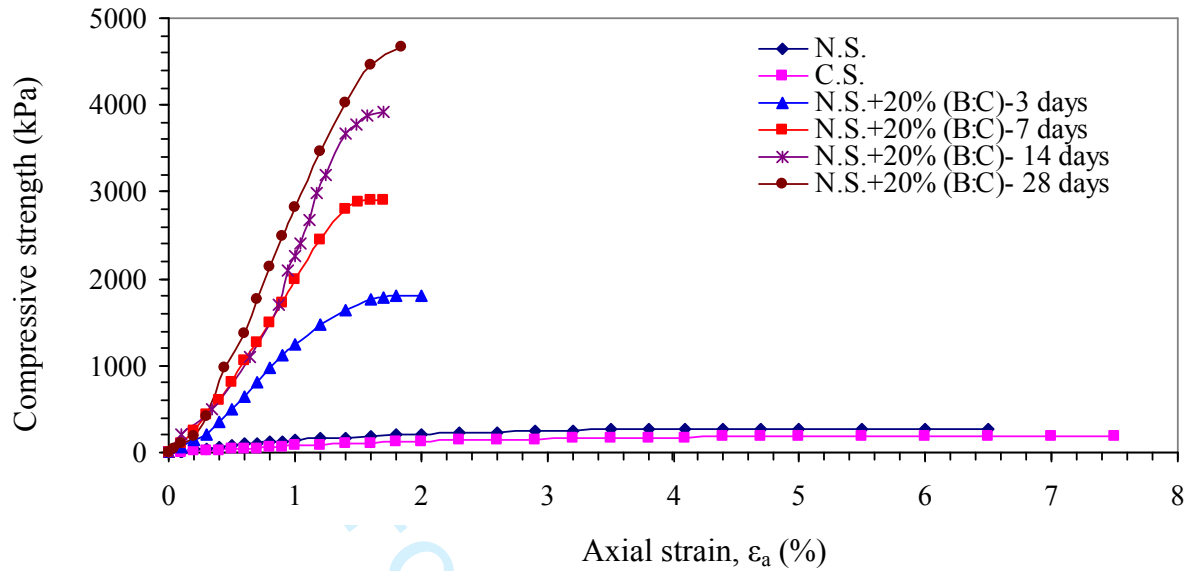


Fig.2. Stress-strain curves for the natural soil, contaminated soil and natural soil with 20% bentonite-cement (ratio 1:1) at different curing times. N.S.= Natural soil, C.S.= Contaminated soil, B=bentonite, C=Cement.

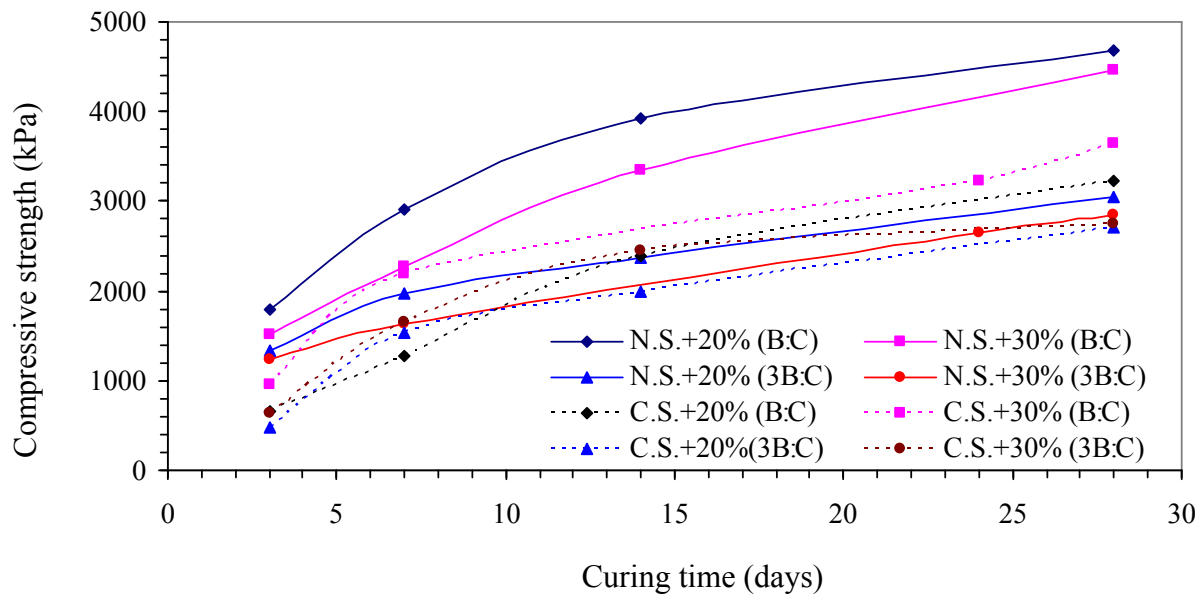
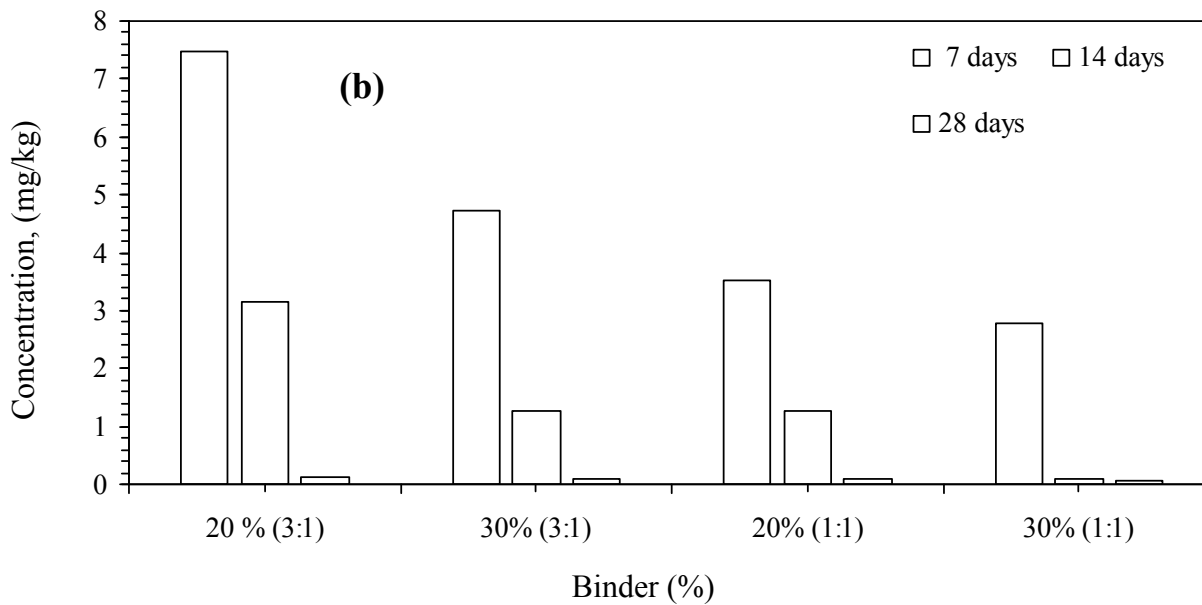
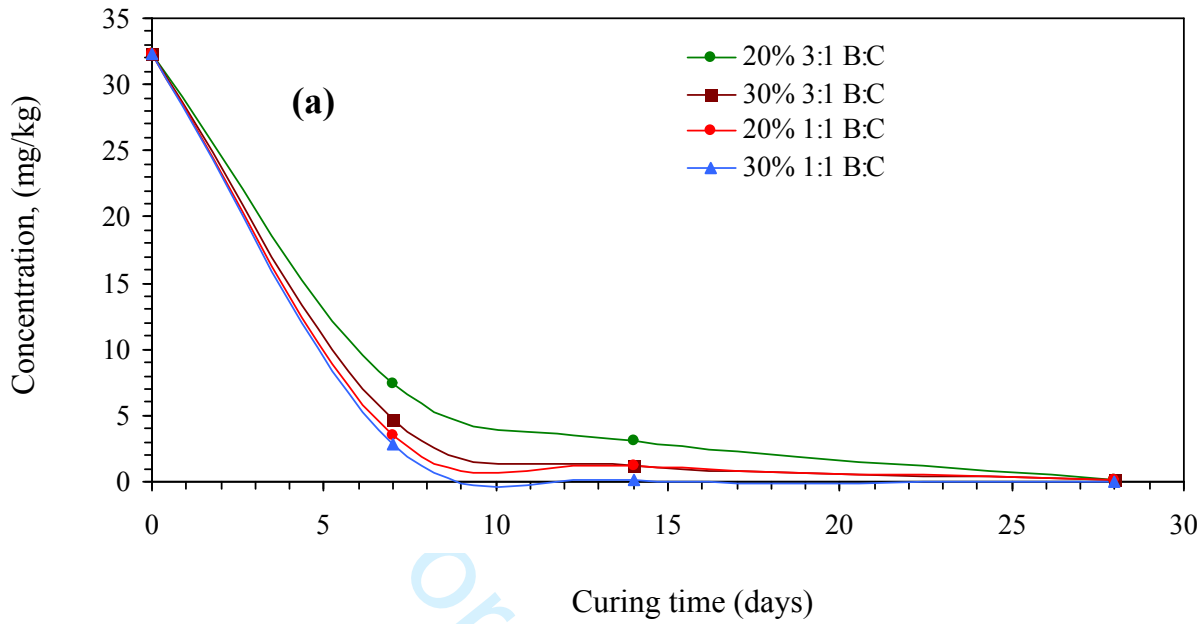


Fig.3. Variations of final strength of the natural soil and contaminated soil alone and with bentonite-cement binders with different ratios (1:1 and 3:1) with curing time for different percentages of binders.



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Fig.4. Variations of the concentration of phenanthrene versus (a): curing time, (b): percentages of binder with ratios of (1:1) and (3:1). B=Bentonite, C=Cement.

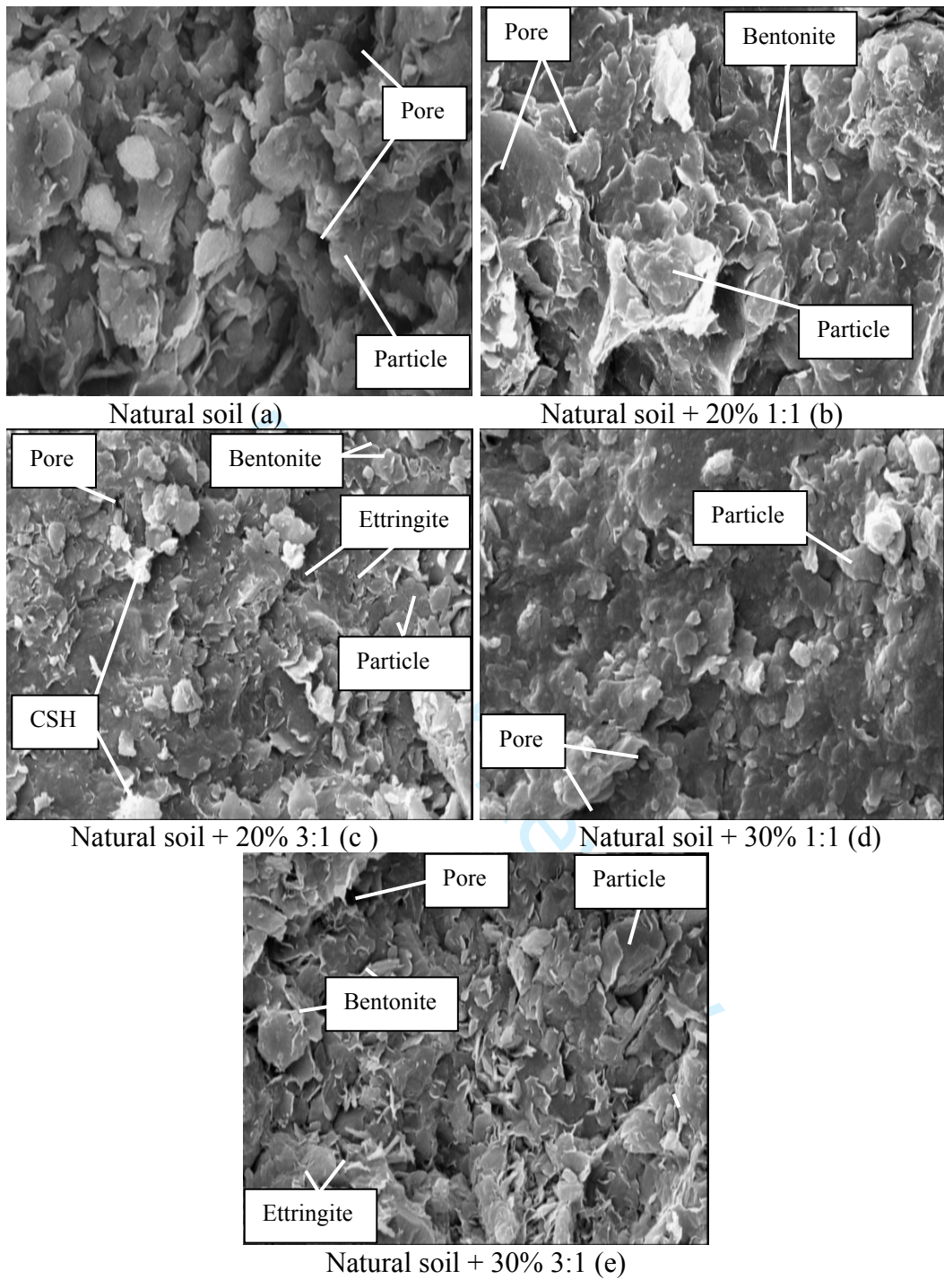


Fig.5. Micrographs for the natural soil and the mixture of natural soil with 20 and 30% agent with different ratios (1:1 and 3:1) at curing time of 28 days.

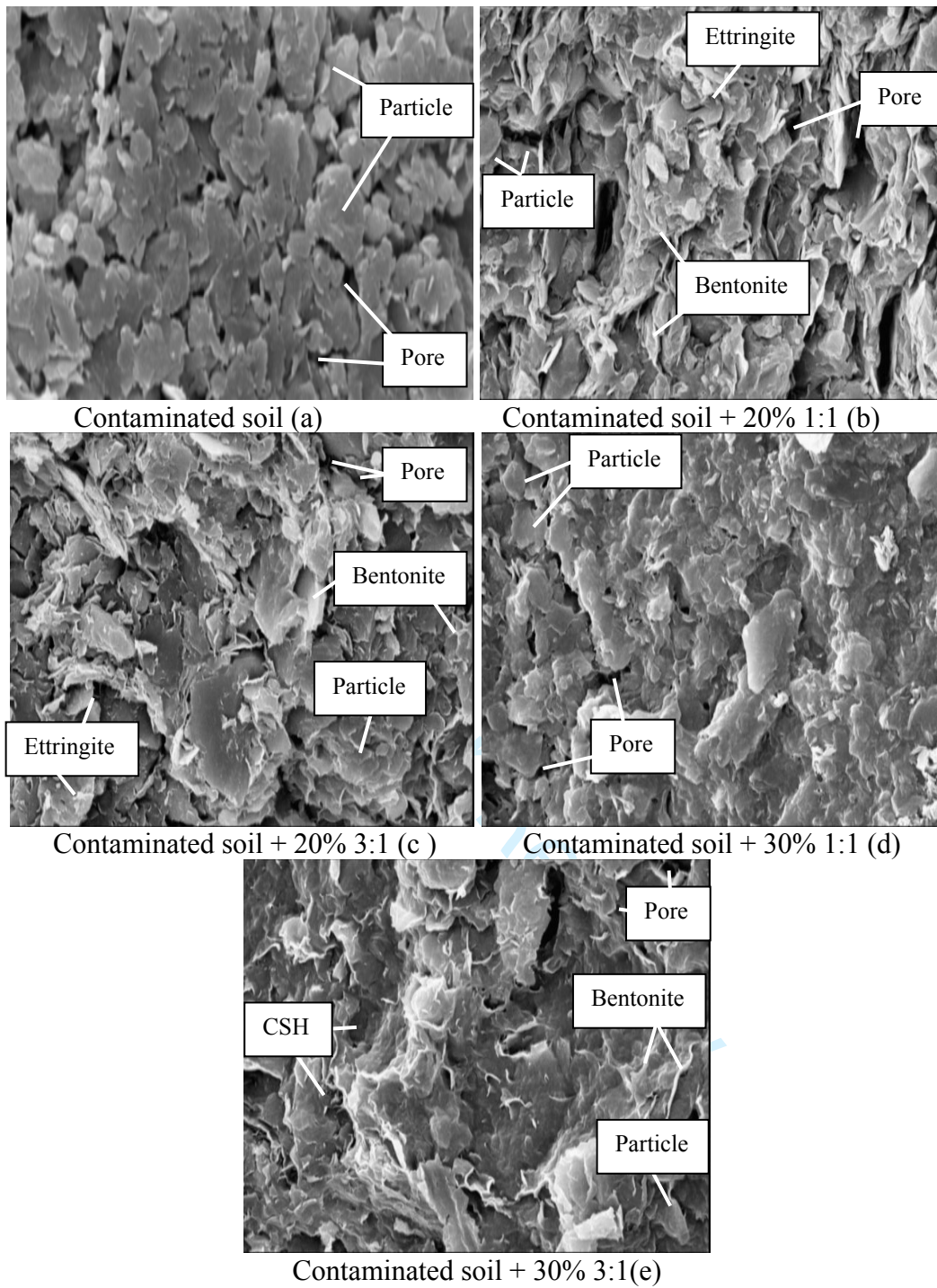


Fig.6. Micrographs for the contaminated soil and mixture of contaminated soil with 20 and 30% agent with different ratios (1:1 and 3:1) at curing time of 28 days.

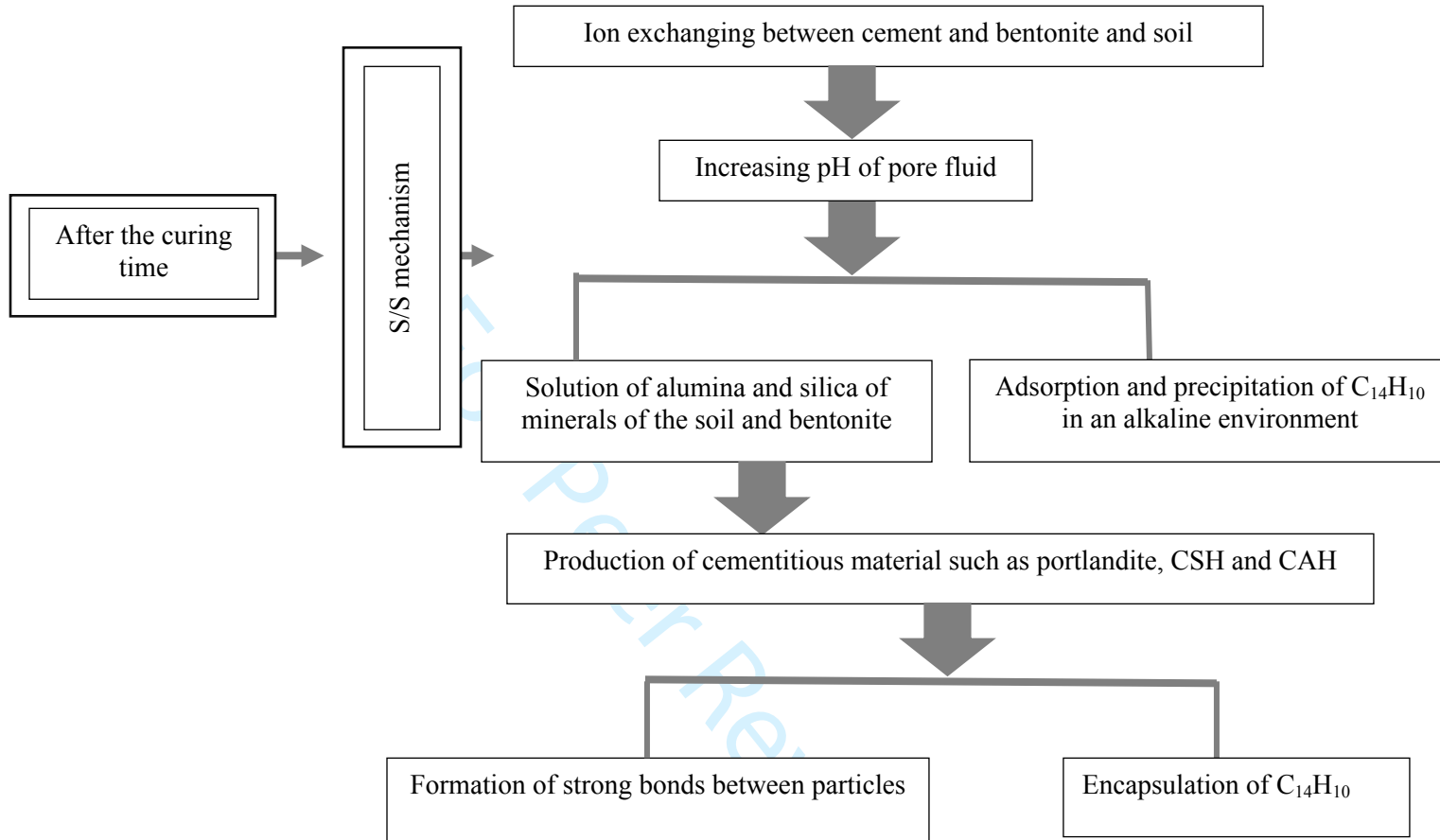


Fig.7. Schematic diagram for the mechanism of stabilization and solidification.

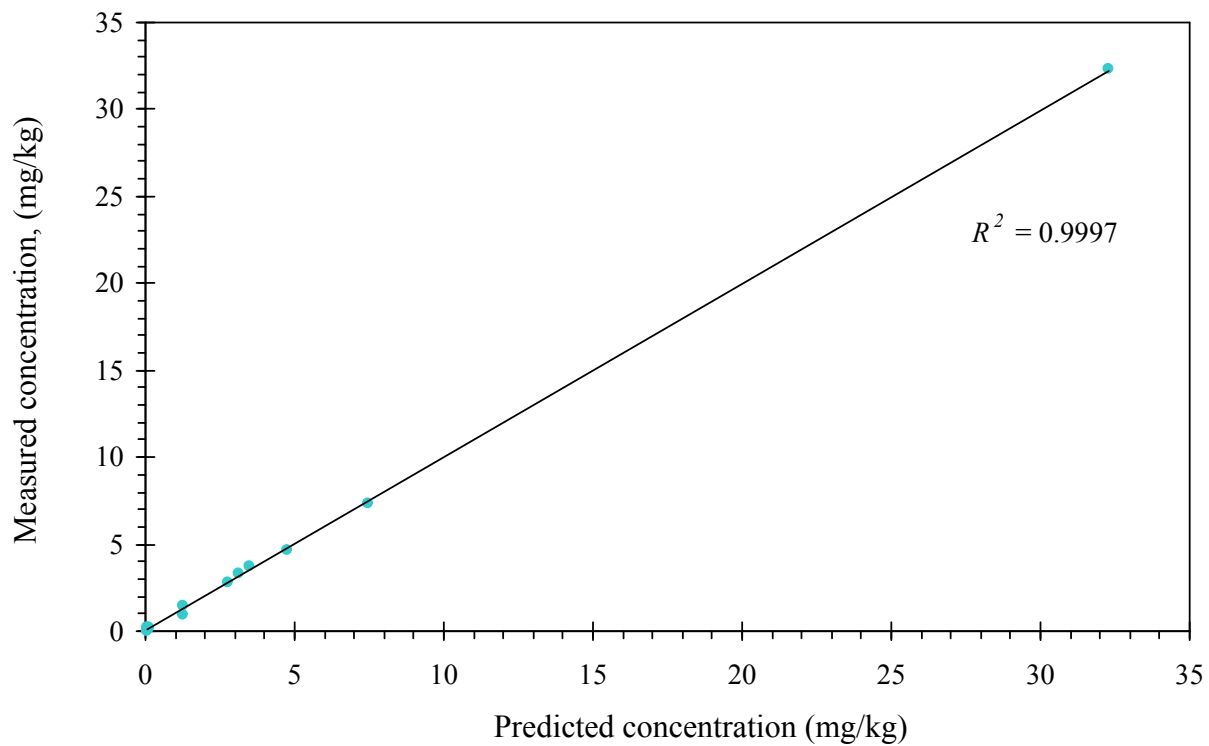


Fig.8. Variations of the measured concentrations against predicted ones

Table 1. Physical and mechanical properties of soil

Property	Standard Designation	Value
Specific gravity, G_s	ASTM D 854-10	2.70
<i>Particle distribution</i>		
Gravel (%)		0.0
Sand (%)		2.0
Silt (%)		45.0
Clay (%)		53.0
<i>Consistency limits</i>		
Liquid limit, LL (%)	ASTM D 4318-10	47.0
Plastic limit, PL (%)	ASTM D 4318-10	26.0
Plastic index, PI (%)	ASTM D 4318-10	21.0
Shrinkage limit, SL (%)	ASTM D 427-04	16.0
USCS classification	ASTM D 2487-11	CL
<i>Compaction characteristics</i>		
Optimum water content, w (%)	ASTM D 698-07e	18.5
Maximum dry unit weight, γ_{dmax} (kN/m ³)		16.77

Table 2. Chemical composition of the soil

Chemical component	Amount	Chemical component	Amount
pH	8.0	Cl ⁻ (meq/l)	60.0
EC ^a (dS/m)	10.74	HCO ₃ ⁻ (meq/l)	4.0
Na ⁺ (meq/l)	42.0	SO ₄ ²⁻ (meq/l)	83.0
Ca ²⁺ (meq/l)	24.0	CaCO ₃ (%)	10.2
Mg ²⁺ (meq/l)	10.0	O.C. ^b (%)	0.05

a- Electrical Conductivity

b- Organic content

Table 3. Properties of cement

Properties	Standard designation	Value
Normal consistency (%)	ASTM C 187-10	29.2
Primary setting time (min)	ASTM C 191-08	108
Final setting time (min)	ASTM C 191-08	180
Compressive strength (MPa)	ASTM C 109-08	
7 days		23.0
28 days		34.0
Tensile strength (MPa)	ASTM C 190-85	
7 days		1.6
28 days		2.4
Flexure strength (MPa)		
7 days		3.1
28 days		4.2

Table 4. Physical and chemical properties of Phenanthrene

Properties	Value
Chemical formula	$C_{14}H_{10}$
Appearance	Colorless to yellow
Molecular weight	178.23 g/mol
Density	1.18 g/cm ³
Dielectric constant	2.72
Water solubility	1.15 mg/l
Melting point	97-100 ⁰ C
Boiling point	336 ⁰ C

Table.5. Atterberg limits and compaction parameters for natural soil and contaminated soil with different percents of bentonite and cement

Materials	LL (%)	PL (%)	PI (%)	$\gamma_{d(max)}$ (kN/m ³)	$w_{(opt)}$ (%)
N.S.	47.0	26.0	21.0	16.77	18.5
N.S.+20% (B:C)	53.0	30.0	23.0	17.44	17.0
N.S.+30% (B:C)	56.0	33.0	23.0	17.3	16.5
N.S.+20% (3B:C)	62.0	33.0	29.0	16.8	19.2
N.S.+30% (3B:C)	73.0	41.0	32.0	16.5	18.85
C.S.	50.0	27.0	23.0	16.8	16.0
C.S.+20% (B:C)	55.0	31.0	24.0	16.0	21.8
C.S.+30% (B:C)	55.0	36.0	19.0	14.92	23.2
C.S. +20% (3B:C)	66.0	34.0	32.0	14.90	25.8
C.S.+30% (3B:C)	73.0	39.0	34.0	14.6	27.0

N.S.=Natural Soil, C.S.= Contaminated Soil, B=Bentonite, C= Cement